TRACE METALS IN ATMOSPHERIC PARTICLES: CHEMICAL SPECIATION, SOURCE IDENTIFICATION, BIO-ACCESSIBILITY AND HEALTH RISK ASSESSMENT

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Airborne particulate matter contains mixture of solid particles and liquid droplets that are suspended in the air for long periods of time, varying in size, composition, and origin (Dockery et al, 1993, Bascom et al, 1996). They can be composed of acids, metals, organic compounds, soil or dust particles and are produced by both natural and anthropogenic sources(USEPA, 2013). Natural sources of airborne particulate matter are forest fires and volcanic eruptions while anthropogenic sources include industrial processes such as mining, metal smelting, oil combustion, waste incineration, transportation and agricultural activity(Manalis et al, 2005,Valavanidis et al, 2006, da Silva et al, 2008, Tian et al, 2011, 2012a, b).They play important roles in environmental issues related to global and regional climate, air quality, visibility degradation, chemistry of the atmosphere, and human health. They affect the climate by altering the amount of solar radiation reaching the earth's surface and acting as cloud condensation nuclei or altering cloud particle size and number. They reduce visibility by scattering and absorption of solar radiation.Atmospheric particulate matter isharmful for human health with regard to respiratory and cardiovasculardiseases, morbidity and mortality (WHO, 2014). Epidemiologicalstudies have indicated that the morbidity of lung cancer in human beings was closely related to the pollution level of totalsuspended particles in urban atmospheric environment(Wang, 2002). Acute and chronic exposure to ambient particulate matter is also closely associated with the aggravation of asthma and highincidence of chronic obstructive pulmonary disease (Wang et al,2013).

Among the atmospheric particulate matter, fine and coarse particulate matter with an aerodynamic particle diameter of $\leq 2.5\mu m$ and $\leq 10\mu m$ referred to as $PM_{2.5}$ and PM_{10} respectively, are of great concern because of its adverse health effects (Sun et al., 2006, Jiao et al., 2012). Fine-particulates such as $PM_{2.5}$ can cause great risk to human health because they can be breathed more deeply into the

lungs and are more toxic than the larger particles and cause morbidity and mortality (Dockery et al, 1993, Bascom et al, 1996, USEPA, 2013). These fine particles come in the atmosphere due to combustion of residential fuels for heating and cooking, smoking, vehicles, construction and renovation, solvents and surface coating and may contain several elements.Beside the mass concentration and the particle size (Dockeryet al, 1993,Oberdörster et al, 1995, Schwartz et al, 1996), thechemical composition and especially the concentration of potentialtoxic metals of aerosols play a decisive role for the assessment ofatmospheric pollution and its hazards to human health (Shi et al,1994, Dreher et al, 1997, Kodavanti et al, 1997, Witholt et al,2000, Zereini et al, 2001, Gwiazda et al, 2002, Chillrud et al,2004).

Concentration of metals in airborne particulate matter can vary from one place to another place depending on the nature and local sources, weather conditions, topography, temperature and time. Crustal elements, such as Na, Mg, Al, K, Ca, Sc, Ti, V, Mn, Fe, As, and Ba accountfor the total natural emissions of metals to the atmosphere (Cong et al., 2011). Industrial metallurgical processes may emit into the atmosphere, metals like As, Cd, Cu, Ni, and Zn, whereas the combustion of fossil fuels is the principal anthropogenic source of Be, Co, Hg, Mo, Ni, Sb, Se, Sn, V, As, Cr, Cu, Mn, and Zn (Pacyna, 1998). Traffic pollution emits the metals Pb, Fe, Cu, Zn, Cr, Sn, Sb, Ni, and Cd. Tire rubber abrasion is a major source of Zn.

Metal compounds are an important class of particulate matter. It is well known that $PM_{2.5}$ has high concentration of many potentially toxic metals that can be incorporated into the human body through inhalation and have adverse physiological effects (Mohanraj et al, 2004). Additionally, metal elements absorbed to particulate matter in the atmosphere may travel long distances and be deposited to soils, water bodies and plant leaves via wet and dry deposition and pose a potential risk to the local environment (Li et al, 2013). The mechanisms involved in adverse health effects caused by inhaled particles are not well understood. However, it has been proposed that the damage to health can be

derived from metal-mediated generation of reactive oxygen species (ROS),which can cause severe oxidative stress within cells or tissues through the oxidation of nucleic acids, proteins, and lipids. Transition metals such as Co, Cu, Cr, Fe, Ni and V have been known to play a role in redox reactions under certain conditions causing oxidative damage to biomolecules. Iron can be especially involved in the generation of highly reactive hydroxyl radical (OH•**)** in the presence of O_2 (or H_2O_2) and/or of a reductant such as ascorbate or cysteine. Ascorbic acid may also be involved in the production of ROS since the human lung epithelial lining fluid contains about 160 μmol L^{-1} of such acid (Song et al, 2003). Recently, Vidrio et al. (2009) quantified OH• in extracts produced from the extraction of $PM_{2.5}$ using a surrogate lung fluid (SLF). The results indicated that dissolved iron could account for the majority of OH• produced in most of the $PM_{2.5}$ extracts.

A great deal of research has focused on the metal composition of atmospheric suspended particulate matter. However, determination of metal levels is usually limited to estimating the quantity of total suspended particles (TSPs), PM_{10} or $PM_{2.5}$ particles. Although these measurements can give some indication of the general pollution level in an area, they do not provide any informationon the size distribution or on the chemical speciation of the metals. Measurements of total metal content are a poor indicator of metal bioavailability, mobility or toxicity. Trace metals associated with air-borne particulate matter have different speciation or fractions that exhibit different bioavailability and potential risk to human beings. A labile fraction of the particle-bound metals is considered to be more readily available to environmental receptors and hence possesses greater environmental risk than the resistant fraction. The trace metal contents of airborne fine form and in particular the water-soluble fractionare correlated positively with observed pulmonary toxicity (Adamson et al., 2000; Sun et al., 2001). Hencethe determination of specific chemical forms, or the nature of binding, is much more valuable than the determination of the total metal content, since the toxic effects and the geochemical pathways of elements are determined mainly by their mobile species (Quevauviller et al., 1998). Knowledge of the chemical speciation of the particles is vital in understanding the effects on human

health.There is growing recognition that particulate standards based on TSP or PM_{10} alone are insufficient (EPA, 1999). The degree of respiratory penetration and retention is a direct function of the aerodynamic particle size. Particles <1–2 mm in aerodynamic diameter are predominantly deposited in the alveolar regions of the lung where the adsorption efficiency for trace elements is 60–80% (Infante and Acosta, 1991) and can affect lung physiology, especially if the particles contain biologically available toxic metals.

In India, studies concerning metals in particulate matter have focused mainly on the determination of the total concentrations of heavy metals, their seasonal and spatial variations and identification of their sources (Lakhani et al, 2008, Kulshrestha et al, 2009, Pramod et al, 2012, Kulshrestha et al, 2014) but have not considered the metal fractionation. Therefore this work has been planned to study the chemical fractionation and distribution of heavy metals in $PM_{2.5}$ and PM_{10} collected from a rural and urban site in Agra with the following objectives

1. Determination of concentrations of major crustal elements (Na, K, Ca, Mg) and some heavy metals (Si, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn,V, As) in $PM_{2.5}$ and $PM_{10.}$
2. Investigation of the seasonal and spatial pollution characteristics of these elements.
3. Identification of probable sources on the basis of metal concentrations.
4. Evaluate the mobility potential and environmental risk based on the metal fractionation distribution.

Methodology:-

For this study sampling will be performed at a ruraland urban site of Agra.Samples of $PM_{2.5}$ and PM_{10} will be collected on pre-weighed and desiccated 47 mm quartz fiber filters (Pallflex) by Fine Particulate Sampler (EnvirotechAPM 550). The sampling will be done for 24 hours at a flow rate 16.6 L/min. Sampling will be done twice a week.After sampling the filters will be again desiccated and weighed till constant weight.For the analysis of metals, filter paper will be digested by an acid

treatment. Each filter will be folded and placed in beaker then 5 ml of HNO_3 (12N) will be added, covered with a watch glass and heated slowly. Before complete evaporation, 5ml of acid will be again added, covered with a watch glass and heated to obtain refluxing action till a clear solution will be obtained. The solution will be filtered using 0.45 µm pore size nylon membrane filters. The filtrate will be transferred to 50 ml volumetric flask and made up with de-ionized water. The metallic elements will be analyzed by Atomic Absorption Spectrometer.

Few representativesamples (10 to 15) of $PM_{2.5}$ and PM_{10} in each season will be sequentially extracted in order to establish the distribution of metals among water soluble, environmentally mobile, bound to carbonate and oxides and environmentally immobile (bound to organic matter and silicates) fractions to determine metal bioavailability, mobility and toxicity.The sequential extraction proceduredeveloped by Fernandez Espinosa et al. (2002) will be followed.The reagents and operational conditions to be followed in each step are given in Table-1. This procedure fractionates the PM_{10} and $PM_{2.5}$-bound metals intofourfractions:

(a) Highly mobile, soluble and exchangeable metals which are weakly bound to the matrix (F1)

(b) Mobile elements mainly bound to carbonates and oxides (F2) and

(c) Less mobile metals bound to organic matter, oxidizable and sulfidic metals (F3) and

(d)Most immobile metals mainly bound to silicates and organic matter (F4).

The elements of high toxicity are highly concentrated in both mobile fractions, indicating that these elements have a direct impact on the environment and on the health of the exposed population.

Following each extraction step, the extracts will be separated from the residues by centrifuging for 15 min at 4500 rpm. The supernatant will be decanted from the residuals and transferred to a Teflon beaker, and then heated until 1-2 mL of solution remains. This solution will be diluted to 10 mL with 2% HNO_3, and stored in a polyethylene bottle at 4 ºC until analysis. Before applying the next step of the extraction scheme, the remaining dust loaded filter material will be dried in a water bath. After the

third extraction step, the residuals will be digested using a mixture of HNO_3, HCl and $HClO_4$.Concentration of metals in each fraction will be determined by ICP-AES. Reagent blanks and filter blanks will be routinely analyzed in between samples to check for contamination.

Metallic fraction	Mobility	Reagent	Experimental condition
F1. Soluble and exchangeable metals	Highly mobile	15mL H_2O (pH= 7.4)	3h shaker agitation at room temperature
F2. Carbonate, oxides and reducible metals	Mobile	10mL $NH_2OH.HCl$ 0.25M at pH =2.0	5h shaker agitation at room temperature
F3. Bound to organic matter, oxidizable and sulphidic metals	Less mobile	7.5 mL H_2O_2 30% + 7.5 mL H_2O_2 30% + 15mL NH_4OAc 2.5M at pH=3	Shaker agitation at 95°C until near dryness + repetition + Shaker agitation for 90 min at room temperature
F4. Residual metals	Not mobile	10mL (HNO_3:HCl:$HClO_4$) (6:2:5)	Shaker agitation for 5h at 95°C

Spatial and seasonal characterization and source identification will be attempted by statistical methods like Correlation, Regression, Analysis of Variance, Enrichment Factor and Data Reduction Methods such as Principal Component Analysis.

Health Risk Assessment:Health risk assessment is useful for estimating the occurrence of adverse health effects in children and adults resulting from the direct inhalation of atmospheric particulates(Hu et al., 2012; Taner et al., 2013). The risk assessment model mainly involves exposure

assessment and risk characterization. The reference concentration (RfC) and inhalation unit risk (IUR) will be used for the risk characterization for elements that induce non-carcinogenic but toxic effects (metals like Al, As, Cd, Cr, Mn, Ni, Se, and V) and carcinogenic elements (As, Cd, Cr, Ni, and Pb), respectively. The exposure concentration (EC) of non-carcinogenicelements and carcinogenic elements will be estimatedto assess the risk posed by metals in particulate matter via inhalation (US EPA, 2011a). The EC ofthe non-carcinogenic elements and carcinogenic elements will be calculated as follows:

EC = [C × ET × EF × ED]/ [AT]

where, C is the exposure point concentration (metal concentration in $PM_{2.5}$ at the time of exposure),ET is theexposure time (generally considered as 8h/day),EF isthe exposure frequency (considered as 250day/year) , ED isthe exposure duration (6 years for children and 24 years for adults)and AT is the average time of exposure,which for non-carcinogens will be calculated using AT = ED × 365days ×24 h/day and for carcinogens will be calculated usingAT = 70 year × 365 days/year × 24 h. All parameters used in the calculation of EC can be found in report published by the US EPA (US EPA, 2011a).

The RfC and IUR were obtained from the US EPA website (US EPA, 2011b) (http://www.epa.gov/region9/superfund/prg/index.

html)(http://www.epa.gov/region9/superfund/prg/index.html)].

The risk characterization will be determined according to the exposure dose assessment. For non-carcinogenic elements, the Hazard Quotient (HQ) will be calculated as follows (US EPA, 2011b)

HQ= EC/(RfC×1000 $\mu g mg^{-1}$)

The Excess Lifetime Cancer Risk (ELCR) will be calculated to evaluate the overall cancer risk as follows:

ELCR= IUR×EC

Where, HQ= Hazard Quotient

EC= Exposure concentration

Bioavailability Assessment- Bioavailability is the percentage of the soluble element content extracted which is supposed to be easily assimilated to living beings system by water with respect to its total content in particulate matter (Smichowski et al., 2005). It indicates that the soluble fractions are labile and completely bioavailable. The fraction of the trace metals which are readily bioavailable once inhaled to the respiratory system causes the highest risk to human health.

Bioavailability index (BI) will be calculated by following equation.

$BI = C_S / C_T$

Where, C_S and C_T are the soluble and total concentrations of metal, respectively.

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